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Reactive extraction of lactic acid using alamine 336 in MIBK: equilibria and kinetics

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Abstract

Lactic acid is an important commercial product and extracting it out of aqueous solution is a growing requirement in fermentation based industries and recovery from waste streams. The design of an amine extraction process requires (i) equilibrium and (ii) kinetic data for the acid–amine (solvent) system used. Equilibria for lactic acid extraction by alamine 336 in methyl-*iso*-butyl-ketone (MIBK) as a diluent have been determined. The extent to which the organic phase (amine + MIBK) may be loaded with lactic acid is expressed as a loading ratio, $z = [\text{HL}]_o/[\text{B}]_{i,o}$. Calculations based on the stoichiometry of the reactive extraction and the equilibria involved indicated that more lactic acid is transferred to the organic phase than would be expected from the (1:1) stoichiometry of the reaction. The extraction equilibrium was interpreted as a result of consecutive formation of two acid–amine species with stoichiometries of 1:1 and 2:1. Equilibrium complexation constant for (1:1) and (2:1) has been estimated. Kinetics of extraction of lactic acid by alamine 336 in MIBK has also been determined. In a first study of its kind, the theory of extraction accompanied by a chemical reaction has been used to obtain the kinetics of extraction of lactic acid by alamine 336 in MIBK. The reaction between lactic acid and alamine 336 in MIBK in a stirred cell falls in Regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film. The reaction has been found to be zero order in alamine 336 and first order in lactic acid with a rate constant of 1.38 s^{-1} . These data will be useful in the design of extraction processes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lactic acid; Reactive extraction; Alamine 336; MIBK; Equilibria; Kinetics

1. Introduction

Lactic acid is a commodity chemical utilized in the food, chemical and pharmaceutical fields. Lac-

tic acid is an important chemical, which can be converted to ethanol, propylene glycol, acrylic polymers and polyesters. In particular an increasingly interesting application is the use of lactic acid as a monomer for the synthesis of biodegradable homopolymers and copolymers (Buchta, 1983; Datta et al., 1995). Lactic acid is a raw material for the production of biodegradable

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polylactic acid. A growing demand for biodegradable polymers, both substitutes for conventional plastic materials and new materials of specific uses such as controlled drug delivery or artificial prostheses, draws attention to improved conventional processes for lactic acid production (Lipinsky and Sinclair, 1986).

Recovery of lactic acid from aqueous solutions is a growing requirement in fermentation based industries and recovery from waste streams. Lactic acid can be produced by the fermentation of biomass. However the fermentation broth has a low concentration ($< 10\%$) of lactic acid due to a product inhibition of the biological process. The traditional recovery process of lactic acid from fermentation broth is quite complicated. Isolation of this acid from dilute wastewater or fermentation broths is an economic problem since the vaporization of water consumes much energy and a direct upgrading of the wastewater by evaporation is inefficient. Lactic acid is non-volatile and hence distillation is not useful. In conventional processes, lactic acid has been recovered from the fermentation broth by precipitation of calcium lactate with calcium hydroxide. In this recovery scheme, calcium lactate is precipitated, recovered by filtration and converted to lactic acid by addition of sulfuric acid. The dilute lactic acid product is then sequentially purified using activated carbon, evaporation and crystallization. These separation and final purification stages account for up to 50% of the production costs (Chaudhuri and Pyle, 1992; Eyal and Bressler, 1993). Thus, this method of recovery is expensive and unfriendly to the environment as it consumes lime and sulfuric acid and also produces a large quantity of calcium sulfate sludge as solid waste (Shreve and Brink, 1977). Allowing accumulation of lactic acid product in fermentation broth inhibits further product formation. Reactor productivities are low and the products are obtained in the dilute form. The effects of end product inhibition can be reduced by in situ removal of lactic acid from fermentation broth by several methods.

A number of processes for lactic acid recovery from fermentation broth without precipitation have been studied and reported in the literature: solvent extraction (Wardell and King, 1978;

Baniel et al., 1981; Kertes and King, 1986; Tamada et al., 1990a,b; Yabannavar and Wang, 1991; King, 1992; Tik et al., 2001) membrane bioreactor (Moueddeb et al., 1996; Jaung and Huang, 1997; Tong et al., 1998), liquid surfactant membrane extraction (Baniel, 1982; Sirman et al., 1991), adsorption (Kaufman et al., 1994), direct distillation (Cockrem and Johnson, 1991), electro-dialysis (Hongo et al., 1986; Boyaval et al., 1987; Lee et al., 1998), chromatographic methods (Hauer and Marr, 1994), ultrafiltration (Hauer and Marr, 1994), reverse osmosis (Timmer et al., 1994), drying (Hauer and Marr, 1994), etc.

Reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids (Wardell and King, 1978; Wennersten, 1983). Reactive liquid–liquid extraction has the advantage that lactic acid can be removed easily from the fermentation broth, preventing the lowering of pH. Further, the lactic acid can be re-extracted and the extractant recycled to the fermentation process.

Organic bases or amine extractants can provide much higher equilibrium distribution coefficients (K_D) for extraction of carboxylic acids than conventional solvents. Solvent extraction with tertiary amines has been widely used to recover fractionate metals such as uranium, iron, cobalt, etc. from aqueous solutions. Most of these extractions are essentially ion-exchange extractions, because the amine group is protonated in sufficiently acidic solutions and forms an ion pair with a metal that is present in anionic form (Baniel et al., 1981). Tertiary amine extractants are effective, with K_D strongly dependent upon the nature of the diluent used and the concentration of amine in that diluent (Ricker et al., 1979). The active diluents are usually divided into three classes: active diluents containing chlorine atoms (methylene chloride, 1-chlorobutane, chlorobenzene, chloroform), carbon-bonded oxygen donor active diluents (methyl isobutyl ketone (MIBK), 1-octanol, 1-decanol) and phosphorous-bonded oxygen donor active diluents (tri butyl phosphate) (Han and Hong, 1996).

Tertiary amines are found to be effective in extracting lactic acid and alcohols are among the best diluents, with the additional advantage that a lactic acid ester can be produced after the extraction process is completed (Ratchford et al., 1951; King, 1983). Alamine 336 (mixture of C₈, C₉ and C₁₀ tertiary amines) yields a good combination of high K_D , low solubility in water and good regenerability. The extractant must be diluted with an organic solvent to provide suitable physical properties for use in an extraction process. The diluent also has a strong effect on extraction equilibria (Wardell and King, 1978). The diluted extractant gives much higher K_D values than the pure extractant.

The design of an amine extraction process requires (i) equilibrium and (ii) kinetic data for the acid–amine (solvent) system used. Considerable information on the equilibrium of several acid–amine (solvent) systems is available in the literature. However, no information pertaining to kinetics is available. In view of this it was thought desirable to obtain the kinetics of extraction of lactic acid from aqueous solutions using alamine 336 in MIBK.

This research work reports the liquid–liquid equilibrium data and kinetics for the extraction of lactic acid by alamine 336 (a tertiary amine, with aliphatic chains of 8–10 carbon groups) dissolved in MIBK, as diluents.

2. Materials and methods

2.1. Materials

All the chemicals used (lactic acid, MIBK, sodium hydroxide) were of reagent grade and were used without pretreatment. All solutions of lactic acid were prepared by dissolving lactic acid of analytical purity in distilled water. The initial concentration of lactic acid was varied from 1.6 kmol m⁻³ to 0.088 kmol m⁻³. Comparatively low concentration range was used because in the practical case of acid recovery from fermentation broths, the acid concentrations are not expected to be high.

The reactive component was alamine 336 (straight chain tertiary amine containing C₈–C₁₀ alkyl groups (Henkel Corp., USA) with MIBK as diluent). Alamine was used as supplied.

2.2. Methods

2.2.1. Equilibria

All experiments were carried out at room temperature at 25 °C. Known volumes of aqueous (different concentrations of lactic acid) and organic phases (50 ml each) (both pure MIBK and MIBK containing different concentrations of alamine 336) of known concentrations were equilibrated in a temperature-controlled shaker bath for 24 h. The two phases were allowed to settle for at least 30 min, which was a sufficient time for a complete phase separation (San-Martin et al., 1992). To determine the concentration of lactic acid, the aqueous phase was titrated with 0.1 N NaOH and phenolphthalein as an indicator. The acid concentrations in the organic phase were calculated by mass balance.

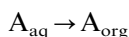
2.2.2. Kinetics

A stirred cell of 0.07 m in diameter and 0.1 m in height, with a flat bottom was used for the kinetic studies (Doraiswamy and Sharma, 1984). Aqueous solution of lactic acid (0.1 m³) of known concentration was first placed in the vessel. The position of the four-blade paddle (0.058 m in diameter and 0.01 mm in width) double stirrer was adjusted to 1 cm below and above the interface. A fixed volume of the organic extractant mixture (0.1 m³) was then added, and stirring was started. Using acid–base titration with 0.1 N NaOH and phenolphthalein as an indicator, acid concentration in aqueous phase was determined periodically. Concentration of lactic acid in the organic phase was determined by mass balance.

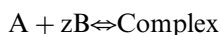
2.3. Theory of extraction accompanied by a chemical reaction

Doraiswamy and Sharma (1984) have given an exhaustive discussion on the theory of extraction accompanied by a chemical reaction (Doraiswamy and Sharma, 1984). Four regimes of extraction

accompanied by reaction have been identified depending upon the physico-chemical and hydrodynamic parameters. When the reaction is reversible the solute has a finite equilibrium concentration in the bulk and the driving force needs to be modified by incorporating the equilibrium concentration. The extraction involves the partitioning of the solute available in the aqueous phase to the organic phase.



The solute A present in the organic phase combines with the organic reactant (amine), B according to



Doraiswamy and Sharma (1984) have given the guidelines for discerning the mechanism in stirred cell. The hydrodynamic factors (as signified by the speed of agitation in a stirred cell) are unimportant in Regimes 1 and 3 whereas the speed of agitation affects the rate of extraction in Regimes 2 and 4. The expressions for the rate of extraction for various regimes are given by Doraiswamy and Sharma (1984). The expression for Regime 3, extraction accompanied by a fast general order chemical reaction occurring in the diffusion film is

$$R_A = [A^*] \sqrt{\frac{2}{m+1} D_A k_{mn} [A^*]^{m-1} [B_0]^n} \quad (1)$$

3. Results and discussion

3.1. Extraction equilibria

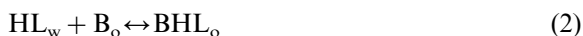
Experiments were carried out to describe the physical and chemical equilibria for lactic acid.

There is only a very slight effect, if any, of temperature in the range of 20–90 °C on the distribution ratio of lactic acid into alcohols, ketones, diethyl carbinol and ethers (Kertes and King, 1986). The physical equilibrium distribution isotherm was measured at 25 °C in MIBK. The results are shown in Fig. 1.

The chemical equilibrium distribution isotherms were measured at 25 °C for alamine 336 concentrations of 20, 30 and 40% v/v in MIBK. The

chemical equilibrium isotherms are shown in Fig. 1. It was observed that extraction efficiency increased with an increase in alamine 336 concentration. San-Martin et al. (1992, 1996) have reported that the degree of extraction increased up to a concentration of 40% v/v of the alamine 336 and then remained constant (San-Martin et al., 1992, 1996).

The reactive liquid–liquid extraction of lactic acid (HL) with the tertiary amine alamine 336 (B) gives a reaction complex (BHL) which remains largely in the organic phase and may be represented by:



The distribution coefficient, K_D is defined by:

$$K_D = [HL]_o / [HL]_w \quad (3)$$

Distribution coefficients obtained by a statistical analysis of the equilibrium data at low concentration of lactic acid for various alamine concentrations in MIBK are given in Table 1.

A quantitative interpretation of the equilibrium for the acid–amine extraction may be defining by equilibrium complexation constant, K_E as:

$$K_E = [BHL]_o / [HL]_w [B]_o \quad (4)$$

The concentration of free amine in the organic phase would be:

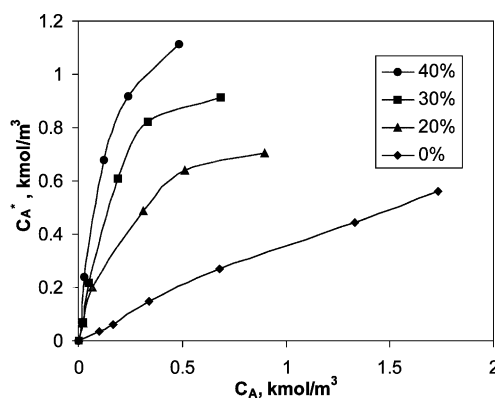


Fig. 1. Equilibrium isotherms for reactive extraction of lactic acid with various concentrations of alamine 336 in MIBK. ●, 40% v/v alamine 336 in MIBK. ■, 30% v/v alamine 336 in MIBK. ▲, 20% v/v alamine 336 in MIBK. ◆, 0% v/v alamine 336 in MIBK.

Table 1

Distribution coefficient for the lactic acid extraction with various concentrations of alamine 336 in MIBK

% Alamine 336	Distribution coefficient (K_D)
0	0.31
20	0.72
30	2.68
40	4.24

$$[B]_o = [B]_{i,o} - [BHL]_o \quad (5)$$

If 1:1 lactic acid–amine 336 complex is formed then $[HL]_o = [BHL]_o$,

$$\log K_D = \log K_E + \log[B]_o \quad (6)$$

If the former assumption is valid, a plot of $\log K_D$ versus $\log[B]_o$ should yield a straight line with a slope of unity. As shown in Fig. 2 the slope is far less than unity (0.2), which implies that the organic phase extracts more acid than would be expected on the basis of 1:1 complex. Hence, the extraction equilibrium of the lactic acid is not adequately represented by Eq. (2).

Though the exact nature of the chemistry involved in the uptake of extra acid is known, and, in spite of the obvious non-ideality of the organic phase, distribution data can be interpreted by a set of equilibria involving the formation of complexes with n acid molecules and one amine molecule (Tamada et al., 1990a,b):

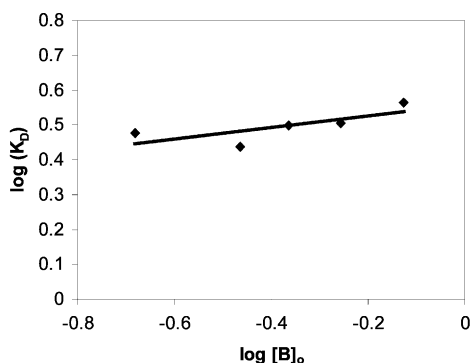


Fig. 2. Distribution coefficient of lactic acid in alamine dissolved in MIBK as a function of free amine concentration in organic phase.

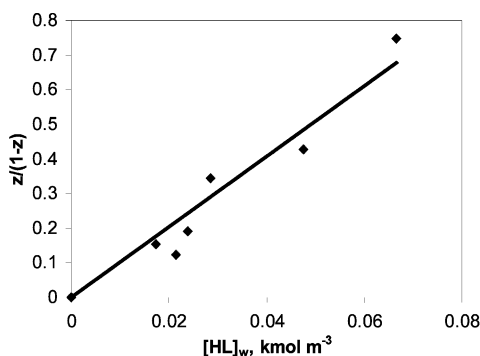
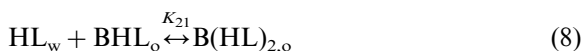


Fig. 3. Plot of $z/(1-z)$ vs. $[HL]_w$ for the estimation of (1:1) lactic acid–amine 336 equilibrium complexation constant.



:



The equilibrium complexation constant for the reaction represented by above equations is:

$$K_{En} = \frac{[B(HL)_n]_o}{[B]_o[HL]_w^n} \quad (10)$$

The extent to which the organic phase (amine 336 + MIBK) can be loaded with lactic acid is expressed as the loading ratio, z ;

$$z = \frac{[HL]_o}{[B]_{i,o}} \quad (11)$$

The value of z depends on the extractability of the acid (strength of the acid–base interaction) and its aqueous concentration, and is independent of the amine content in an inert diluent (Kertes and King, 1986; Tamada et al., 1990a,b).

The stoichiometry of the overall extraction reaction depends on the loading ratio in the organic phase, z . If the organic phase is not highly concentrated, i.e. at very low loading ratios ($z < 0.5$), the (1:1) complex is formed and a plot of $z/(1-z)$ versus $[HL]_w$ is a straight line whose slope gives the complexation constant K_E in Eq. (4) and K_{E1} in Eq. (10).

$$\frac{z}{1-z} = K_{E1}[HL]_w \quad (12)$$

A straight line of the plot of Eq. (12) is shown in Fig. 3 with a slope of 10.15. Hence, the equilibrium complexation constant for the (1:1) complex at 25 °C for the extraction of lactic acid with alamine 336 dissolved in MIBK, for low concentrations of lactic acid in the organic phase is:

$$K_{E1} = 10.15 \text{ m}^3 \text{ kmol}^{-1}$$

For higher loading ratios, the (2:1) complex is formed, and a plot of $z/(2-z)$ versus $[\text{HL}]_w^2$ should yield a straight line, whose slope gives the complexation constant for the (2:1) complex. K_{E2} is obtained from Eq. (10).

$$\frac{z}{2-z} = K_{E2}[\text{HL}]_w^2 \quad (13)$$

A straight line of the plot of Eq. (13) is shown in Fig. 4 with a slope of 10.13. Hence, the equilibrium complexation constant for the (2:1) complex at 25 °C for the extraction of lactic acid with alamine 336 dissolved in MIBK is:

$$K_{E2} = 10.13 \text{ (m}^3 \text{ kmol}^{-1})^2$$

If the lactic acid concentration is high enough, the (3:1) complex may be formed and a plot of $z/(3-z)$ versus $[\text{HL}]_w^3$ should yield a straight line, whose slope gives the complexation constant for the (3:1) complex. K_{E3} is obtained from Eq. (10).

$$\frac{z}{3-z} = K_{E3}[\text{HL}]_w^3 \quad (14)$$

In this work the complex is not formed because the concentration of lactic acid in the organic

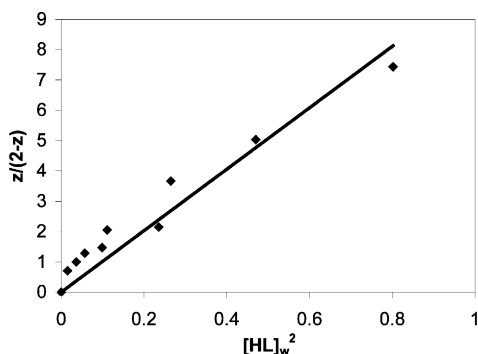


Fig. 4. Plot of $z/(2-z)$ vs. $[\text{HL}]_w^2$ for the estimation of (2:1) lactic acid–alamine 336 equilibrium complexation constant.

Table 2

Concentration range of lactic acid in the aqueous phase at which one of the complexes formed in the organic phase in equilibrium

Complex	Concentration range (kmol m ⁻³)
(1:1)	<0.08
(2:1)	0.09–0.9

phase is not high enough and hence the plot based on Eq. (14) is not considered. This situation is frequently encountered in fermentation processes for production of lactic acid.

Figs. 3 and 4 allow the determination of the concentration range of lactic acid in the aqueous phase at which one of the complexes formed in the organic phase in equilibrium is present in a higher proportion. Results are shown in Table 2.

When lactic acid concentration in the aqueous phase is within the range indicated in Table 2, the equilibrium concentration in the organic phase is high enough to form either the (1:1) or the (2:1) complexes. For the experimental conditions used in this work, lactic acid concentration is not high enough to provide the amount of lactic acid needed in the organic phase so that the (3:1) complex can be formed.

3.2. Kinetics

3.2.1. Physical mass transfer coefficient

The value of physical mass transfer coefficient k_L is required for confirming the regime of extraction. This was obtained by conducting physical extraction (diluent only) of lactic acid from water. For a batch process a differential mass balance yields the following equation,

$$V_{\text{aq}} \frac{dC_{\text{org}}}{dt} = k_L A_c (C_{\text{org}}^* - C_{\text{org}}) \quad (15)$$

Integration of this equation yields,

$$k_L = \frac{V_{\text{aq}}}{A_c t} \int_0^{C_{\text{org}}} \frac{dC_{\text{org}}}{(C_{\text{org}}^* - C_{\text{org}})} \quad (16)$$

The value of k_L evaluated using Eq. (16) for different speeds of agitation is plotted in Fig. 5. The regression relation between the mass transfer

coefficient and the speed of agitation obtained by a statistical analysis data is given below.

$$k_L = 3.5 \times 10^{-5} N^{4.7} \quad (17)$$

The reaction between lactic acid and alamine 336 is reversible, particularly under conditions of high loading in the organic phase. To avoid problems due to this reversibility, only initial rates were considered for evaluation of the kinetics.

3.2.2. Reaction regime

3.2.2.1. Effect of speed of agitation. To find out the reaction regime, discerning the mechanism proposed by Doraiswamy and Sharma (1984) was used. The speed of agitation was varied from 0.65 rev s⁻¹ to 1.4 rev s⁻¹. In this range the liquid–liquid interface was flat and the interfacial area for extraction was equal to the geometric area. Fig. 6 indicates that there was no effect of speed of agitation on the specific rate of extraction, R_A (kmol/m²s). This situation is possible if either Regime 1 or Regime 3 is valid.

3.2.2.2. Effect of phase volume. To differentiate between Regimes 1 and 3, the effect of organic phase volume on the specific rate of extraction was studied. Fig. 7 shows the plot of R_A versus phase volume ratio (volume of organic phase/volume of aqueous phase) at a constant speed of agitation. Evidently, there is no effect of phase volume.

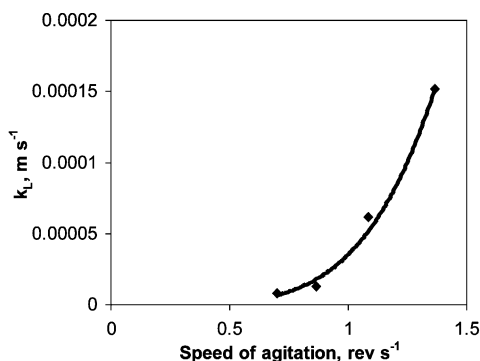


Fig. 5. Effect of speed of agitation on mass transfer coefficient for the extraction of lactic acid with MIBK.

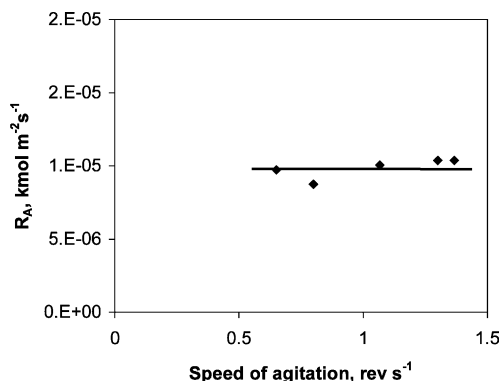


Fig. 6. Effect of speed of agitation on specific rate of extraction for the reactive extraction of lactic acid with alamine 336 in MIBK.

From the above experimental results it can be concluded that the reaction between lactic acid and alamine 336 in MIBK in a stirred cell falls in Regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film.

3.2.3. Order of reaction

3.2.3.1. Order with respect to lactic acid. The aqueous phase lactic acid concentration was varied from 0.1 kmol m⁻³ to 0.25 kmol m⁻³. Fig. 8 shows the effect of organic phase lactic acid concentration on specific rate of extraction, R_A . A regression analysis of the data yielded $m = 1$ (as per Eq. (1)). Thus, the reaction is first order with respect to lactic acid.

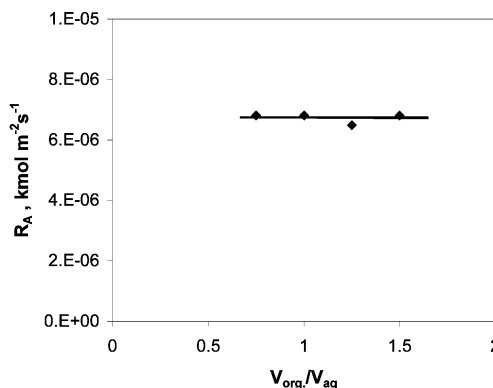


Fig. 7. Effect of phase ratio on the specific rate of extraction for the reactive extraction of lactic acid with alamine 336 in MIBK.

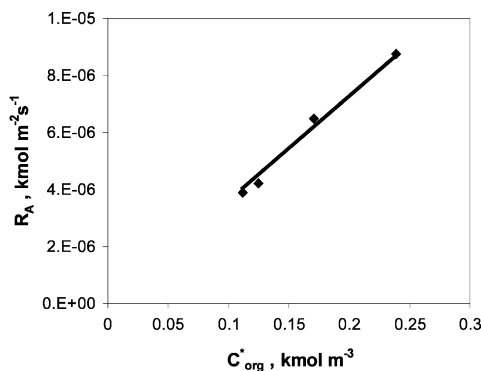


Fig. 8. Effect of initial lactic acid concentration on specific rate of extraction for the reactive extraction of lactic acid with alamine 336 in MIBK.

3.2.4. Order with respect to alamine 336

Fig. 9 shows a plot of the specific rate of extraction of lactic acid against initial alamine 336 concentration in the organic phase. Evidently there is no effect of alamine 336 concentration on the rate of extraction indicating that the reaction is zero order in alamine 336 ($n = 0$ in Eq. (1)).

3.2.5. Rate constant

For $m = 1$ and $n = 0$ (Eq. (1)), the rate expression for the initial part of the extraction is reduced to

$$R_A = C_{org}^* \sqrt{D_A k_1} \quad (18)$$

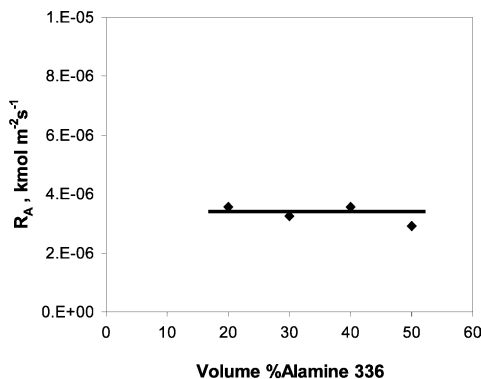


Fig. 9. Effect of initial alamine 336 concentration on specific rate of extraction for the reactive extraction of lactic acid with alamine 336 in MIBK.

The value of D_A was estimated using Wilke–Chang (1955) equation as $1.16 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The data were fitted (Fig. 8) to the above equation to obtain the value of the first order rate constant, k_1 as 1.38 s^{-1} .

To confirm that Regime 3 holds the value of the parameter

$$\sqrt{(D_A k_1)}/k_L$$

was evaluated (Doraiswamy and Sharma, 1984). It was found that for the range of k_L values (Fig. 5)

$$\sqrt{(D_A k_1)}/k_L \cong 8$$

or greater than 3 which is the condition for the validity of Regime 3. Thus, the above mentioned results reflect the true intrinsic kinetics of the extraction process.

It is generally expected that the reaction between a carboxylic acid and amine should be instantaneous, particularly when the reaction takes place in an aqueous medium where both species are likely to be in ionic form. However, in the present case the solubility of lactic acid in the organic phase is higher than that in water. On the other hand the organic amine has practically negligible solubility in the aqueous phase (Ricker et al., 1980). Thus, there is reason to believe that the reaction takes place in the organic phase where ionized species do not exist. This argument further supports the finite kinetics observed in the stirred cell experiments.

4. Conclusion

The extraction of lactic acid from aqueous solutions by alamine 336 dissolved in MIBK was studied. Physical and chemical equilibria for lactic acid extraction by alamine 336 in MIBK as a diluent have been determined. The extent to which the organic phase (amine + MIBK) may be loaded with lactic acid is expressed as a loading ratio, $z = C_{org}/C_B$. Calculations based on the stoichiometry of the reactive extraction and the equilibria involved indicated that more lactic acid is transferred to the organic phase than would be expected from a 1:1 stoichiometry of the reaction.

The extraction equilibrium was interpreted as a result of consecutive formation of two acid–amine species with stoichiometries of 1:1 and 2:1. Equilibrium complexation constants for (1:1) and (2:1) have been estimated.

In the first study of its kind, the theory of extraction accompanied by chemical reaction has been used to obtain kinetics of extraction of lactic acid by alamine 336 in MIBK. The theory of extraction accompanied by a chemical reaction has been used to obtain the intrinsic kinetics of extraction by alamine 336 in MIBK. The reaction between lactic acid and alamine 336 in MIBK in a stirred cell falls in Regime 3, extraction accompanied by a fast chemical reaction occurring in the diffusion film. The reaction has been found to be zero order in alamine 336 and first order in lactic acid with a rate constant of 1.38 s^{-1} . These data will be useful in the design of extraction processes.

Appendix A. Nomenclature

$[A]^*$	equilibrium concentration in organic phase (kmol m^{-3})
A_C	cross sectional area of stirred cell (m^2)
$[B]_{i,o}$	initial alamine concentration in the organic phase (kmol m^{-3})
$[B]_o$	alamine concentration remain in the organic phase (kmol m^{-3})
$[BHL]_o$	(1:1) lactic acid–alamine complex concentration in organic phase (kmol m^{-3})
$C_A, [LH]_w$	lactic acid concentration in aqueous phase (kmol m^{-3})
C_A^*	equilibrium lactic acid concentration in organic phase (kmol m^{-3})
C_{org}	lactic acid concentration in organic phase (kmol m^{-3})
C_{org}^*	equilibrium lactic acid concentration in diluent only (kmol m^{-3})
D_A	diffusivity of solute A (lactic acid) in solvent (MIBK) ($\text{m}^2 \text{ s}^{-1}$)
K_E, K_{E1}	(1:1) lactic acid–alamine equilibrium complexation constant ($\text{m}^3 \text{ kmol}^{-1}$)

K_{E2}	(2:1) lactic acid–alamine equilibrium complexation constant ($\text{m}^3 \text{ kmol}^{-1}$) ²
K_{E3}	(3:1) lactic acid–alamine equilibrium complexation constant ($\text{m}^3 \text{ kmol}^{-1}$) ³
$[HL]_o$	lactic acid concentration in organic phase (kmol m^{-3})
k_1	first order rate constant (s^{-1})
k_L	overall mass transfer coefficient (m s^{-1})
K_D	distribution coefficient
k_{mn}	rate constant for a reaction that is m th order in species A and n th order in species B
N	speed of agitation (rev s^{-1})
R_A	specific rate of extraction of lactic acid ($\text{kmol m}^{-2} \text{ s}^{-1}$)
t	time of extraction (s)
V_{aq}	volume of aqueous phase (m^3)
z	loading ratio ($\text{kmol lactic acid kmol amine}^{-1}$)

References

- Baniel, A.M., Blumberg, R., Hadju, K., 1981. Recovery of acids from aqueous solutions. U.S. Patent 4,275,234.
- Baniel, A.M., 1982. Process for the extraction of organic acids from aqueous solution. EP 0 049 429.
- Boyaval, P., Corre, C., Terre, S., 1987. Continuous lactic acid fermentation with concentrated product recovery by ultrafiltration and electrodialysis. *Biotech. Lett.* 9 (3), 207–212.
- Buchta, K., 1983. Lactic acid. *Biotechnology* 3, 409–412.
- Chaudhuri, J.B., Pyle, D.L., 1992. Emulsion liquid membrane extraction of organic acids. 1. A theoretical model for lactic acid extraction with emulsion swelling. *Chem. Eng. Sci.* 47 (1), 41–48.
- Cockrem, M.C.M., Johnson, P.D., 1991. Recovery of lactate and lactic acid from fermentation broth. USP 5 210296.
- Datta, R., Tsai, S.P., Bonsignore, P., Moon, S.H., Frank, J.R., 1995. Technology and economic potential of poly(lactic acid) and lactic acid derivatives. *FEMS Microbiol. Rev.* 16, 221–231.
- Doraiswamy, L.K., Sharma, M.M., 1984. Heterogeneous reaction: analysis, examples, and reactor design, Vol. 2: Fluid–Fluid–Solid-Reactions, first ed. Wiley, New York, pp. 17–41.
- Eyal, A.M., Bressler, E., 1993. Mini-review industrial separation of carboxylic acid and amino acids by liquid mem-

- branes: applicability, process considerations and potential advantages. *Biotechnol. Bioeng.* 41, 287–295.
- Han, D.H., Hong, W.H., 1996. Reactive extraction of lactic acid with trioctylamine/methylene chloride/*n*-hexane. *Separ. Sci. Technol.* 31 (8), 1123–1135.
- Hauer, E., Marr, R., 1994. Liquid extraction in biotechnology. *Int. Chem. Eng.* 34 (2), 178–187.
- Hongo, M., Nomura, Y., Iwahara, M., 1986. Novel method lactic acid production by electrodialysis fermentation. *Appl. Environ. Microbiol.* 52 (2), 314–319.
- Jaung, R., Huang, R., 1997. Kinetic studies on lactic acid extraction with amine using a microporous membrane-based stirred cell. *J. Membrane Sci.* 129, 185–196.
- Kaufman, E.N., Cooper, S.P., Davison, B.H., 1994. Screening of resins for use in a biparticle fluidized-bed bioreactor for the continuous fermentation and separation of lactic acid. *Appl. Biochem. Biotech.* 45–46, 545–554.
- Kertes, A.S., King, C.J., 1986. Extraction chemistry of fermentation product carboxylic acids. *Biotech. Bioeng.* 28, 269–282.
- King, C.J., 1983. In: Lo, T.C., Baird, M.H.I., Hanson, C. (Eds.), *Handbook of Solvent Extraction*. Wiley-Interscience, New York, 567 pp.
- King, C.J., 1992. Amine-based systems for carboxylic acid recovery. *Chemtech* 5, 285–291.
- Lee, E.G., Moon, S., Chang, Y.K., Yoo, I., Chang, H.N., 1998. Lactic acid recovery using two-stage electrodialysis and its modelling. *J. Membrane Sci.* 145, 53–66.
- Lipinsky, E., Sinclair, S., 1986. Is lactic acid a commodity chemical? *Chem. Eng. Prog.* 82, 26–32.
- Moueddeb, H., Sanchez, J., Bardot, C., Fick, M., 1996. Membrane bioreactor for lactic acid production. *J. Membrane Sci.* 114, 59–71.
- Ratchford, W.P., Harris, E.H., Fisher, C.H., Willits, C.D., 1951. Extraction of lactic acid from water solution. *Ind. Eng. Chem.* 43, 778–781.
- Ricker, N.L., Michaels, J.N., King, C.J., 1979. Solvent properties of organic bases for extraction of acetic acid from water. *J. Separ. Proc. Technol.* 1, 36–41.
- Ricker, N.L., Pittman, E.F., King, C.J., 1980. Solvent extraction with amines for recovery of acetic acid from dilute aqueous industrial streams. *J. Separ. Proc. Technol.* 1 (2), 23–30.
- San-Martin, M., Pazos, C., Coca, J., 1992. Reactive extraction of lactic acid with alamine 336 in the presence of salts and lactose. *J. Chem. Tech. Biotechnol.* 54, 1–6.
- San-Martin, M., Pazos, C., Coca, J., 1996. Reactive extraction of lactic acid with alamine 336. *J. Chem. Tech. Biotechnol.* 65, 281–285.
- Shreve, R.N., Brink, J.A., 1977. *Chemical Process Industries*, fourth ed. McGraw-Hill, New York, pp. 542.
- Sirman, T., Pyle, D.L., Grandison, A.S., 1991. Extraction of organic acids using a supported liquid membrane. *Biochem. Soc. Trans.* 19 (3), 274–279.
- Tamada, J.A., Kertes, A.S., King, C.J., 1990a. Extraction of carboxylic acids with amine extractants. 1. Equilibria and law of mass action modeling. *Ind. Eng. Chem. Res.* 29, 1319–1326.
- Tamada, J.A., Kertes, A.S., King, C.J., 1990b. Extraction of carboxylic acids with amine extractants. 2. Chemical interactions and interpretation of data. *Ind. Eng. Chem. Res.* 29, 1327–1333.
- Tik, N., Bayraktar, E., Mehmetoglu, U., 2001. In-situ reactive extraction of lactic acid from fermentation media. *J. Chem. Tech. Biotech.* 76, 764–768.
- Timmer, J.K.M., Kromkamp, J., Robbertsen, T., 1994. Lactic acid separation from fermentation broth by reverse osmosis and nanofiltration. *J. Membrane Sci.* 92, 185–197.
- Tong, Y., Hirata, M., Takanashi, H., Hano, T., Kubota, F., Goto, M., Nakashio, F., Matsumoto, M., 1998. Extraction of lactic acid from fermented broth with microporous hollow fiber membranes. *J. Membrane Sci.* 143, 81–91.
- Wardell, J.M., King, C.J., 1978. Solvent equilibria for extraction of carboxylic acids from water. *J. Chem. Eng. Data.* 23, 144–148.
- Wennersten, R., 1983. Extraction of carboxylic acid from fermentation broth using solution of tertiary amine. *J. Chem. Tech. Biotechnol.* 33B, 85–94.
- Wilke, C.R., Chang, P., 1955. Correlation of diffusion coefficient in dilute solutions. *AIChE J.* 1, 264.
- Yabannavar, V.M., Wang, D.I.C., 1991. Extractive fermentation for lactic acid production. *Biotech. Bioeng.* 37, 1095–1100.